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Nucleation Induced Nanostructures

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ABSTRACT

Numerical simulations in films and aggregates have repeatedly shown the presence of vibrations during a phase transition and/or the appearance of periodic structures. A phase transition could be controlled and novel nanostructures created by astute manipulation of such phenomena. In order to study the occurrence and effect of wave-like phenomena, the dynamics of a first order phase transition is described using kinetic theory. At a first order phase transition, the initial phase is replaced in time by the new phase on propagation of a density front through the sample. The dynamic stability analysis studies the transition to the uniform phase by propagation of the front and provides the conditions for the formation of transient periodic structures by a local increase of density. The results apply also to spherical geometry and a discussion of cluster dynamics follows the planar case.

INTRODUCTION

In a first order phase transition, the emerging stable phase displaces the original phase by the dynamic process of nucleation and growth. Between the two phases, a contact forms which propagates as an interfacial profile, providing a practical method to produce materials in thin layers. Applications are well known in thin films and coatings of metals, semiconductors and polymer materials for use in electronics, optics and in the surface modification of materials to improve mechanical or chemical properties.[1]

A phase transition could be controlled and novel nanostructures created by excitation of waves. Numerical simulations in films and aggregates have repeatedly shown the presence of vibrations during a phase transition and/or the existence of specific wave-like motions[2-6] which effect the shape, the morphology and the propagation of the interface.

THEORY

In order to study the occurrence and effect of wave-like phenomena, the dynamics of a first order phase transition is described using kinetic theory [7] for the evolution of the probability distribution of particles $f(\mathbf{r}, t)$ or the number density $n(\mathbf{r},t) = nf(\mathbf{r},t)$, n being the total number of particle per volume. The function $n(\mathbf{r}, t)$ measures the probability for a particle to arrive at position $\mathbf{r}$ after a time t and fulfills the equation of continuity:

$$\frac{\partial n(\vec{r},t)}{\partial t} = -\frac{\partial}{\partial \vec{r}} \cdot \vec{j}(\vec{r},t) \tag{1}$$

The evolution of the flux j (r,t) = $n(r,t)$ $v(r,t)$, $v(r,t)$ being the average velocity of the particles of mass m, is described by the dynamic flux equation,

$$\frac{\partial \vec{j}}{\partial t} = -\beta \vec{j} - \frac{1}{m} n(\vec{r},t) \frac{\partial}{\partial \vec{r}} \mu(\vec{r},t) \tag{2}$$

The friction forces of the medium are included in β. We concentrate on the dynamics of a system which, having achieved uniform temperature, is dominated by particle flow. The driving force of the transition is the gradient of the local chemical potential $\mu(r,t)$. The chemical potential is enslaved by the density and in the effective interaction model [8]:

$$\mu(\vec{r},t) = \mu(n) - \frac{\kappa}{2} \Delta n(\vec{r},t) \tag{3}$$

The function μ (n) is the bulk chemical potential, the second term takes local variations of the density into account. The constant κ is related to the range of the interaction potential between particles.

At a first order phase transition, the initial phase is dynamically unstable and is replaced in time by the new stable phase on propagation of a density front through the sample. The transition from the two phase "kink" solution of eq. (1) and (2) , as described below, to the final phase of uniform density is of interest to the dynamics of the phase transition which proceeds by propagation of the front. The velocity of the front, its shape, stability and the structure that is left behind are studied.

RESULTS

In heterogeneous nucleation the phase transition is initiated on the interface. The new emerging phase may grow and replace the initial phase under certain conditions which will be defined by analysis of the dynamic stability for different initial conditions. The dynamic stability analysis will show that the "kink" of density $n(x,t) = n_1$, x $<L(t)$; $n(x,t) = n_0$, x $> L(t)$ is linearly unstable to a long range local increase of density at the surface. The function $L(t)$ determines the boundary between the phases, the initial phase of density n_0 and the new emerging phase of density n_1, and describes the propagation of the kink.

The two kinetic equations are combined by taking the time derivative of (1), inserting (2) and using (3):
$$\frac{\partial^2 \eta}{\partial t^2} = -\beta \frac{\partial \eta}{\partial t} + c_0^2 [\frac{\partial^2}{\partial x^2} \eta(x,t) - \xi^2 \frac{\partial^4}{\partial x^4} \eta(x,t)] \tag{4}$$

The dynamic equation (4) is linear in a small perturbation $\eta(x,t) = n (x,t) - n_0$ for x>0and its derivatives and valid in the region close to the state of density n_0 for x>0 and $\eta(x,t) = 0$ for

$x<0$. The velocity of sound in the initial uniform medium is $c_0^2 = \dfrac{n_0}{m}\dfrac{\partial \mu(n_0)}{\partial n_0}$ and ξ is the density correlation length.

In one possibility, the initial phase wets the emerging phase and the initial conditions are $\eta(x,t=0) = \eta_0 \exp(-q\,x)$, $j(x,0) = 0$. The resulting perturbation is exponential and $\eta(x,t) \propto \exp[-qx + \omega t]$. The left hand side of (4) determines the dispersion relation $\omega(q)$:

$$\omega(q) = \frac{1}{2}(-\beta \pm \sqrt{\beta^2 + F(q)})$$

$$F(q) = 4q^2 c_0^2(1 - \xi^2 q^2) \tag{5}$$

Different behavior is found for different values of wetting layer thickness and a critical length emerges. The critical wave vector is q_c for which Im $\omega(q_c) = 0$ or $1 + F(q_c)/\beta^2 = 0$.

For $q>q_c$, The solution is a damped vibration which causes the initial wetting layer to vanish with time. $\eta(x,t) = \eta_0 \exp[-qx - \beta t/2][\cos(\Omega_q t) - \dfrac{\beta}{2\Omega_q}\sin(\Omega_q t)]$. The dispersion relation of

the elastic vibration is $\Omega_q = \dfrac{1}{2}\sqrt{-\beta^2 - F(q)}$. The kink is dynamically stable, the transition will not be triggered by this small scale perturbation.

For $1/\xi < q < q_c$, the dispersion relation is real and negative and translation sets in. For example for $q \approx 1/\xi$, the perturbation front recedes with a velocity v_ξ and decays with time.

$$\eta(x,t) = \eta_0 \exp[-q(x + v_\xi t)]\exp(-\frac{v_\xi t}{\xi})$$

$$v_\xi = \frac{2c_0^2}{\xi\beta}$$

For $q < 1/\xi$, the dispersion relation is real and positive. For $q\xi \ll 1$, the perturbation front advances with a positive velocity v:

$$\eta(x,t) = \eta_0 \exp[-q(x - vt)]$$

$$v = \frac{c_0^2 q}{\beta}(1 - q^2 \xi^2)$$

For stationary total number of particles, the velocity of the interface dL/dt must be equal to the average flux of the particles normal to the interface [9] and

$$dL/dt = -j_x(L,t) / (n_1 - n_0 - \eta(L,t)) \tag{6}$$

When the density of new phase is larger than that of the initial phase (such as on condensation or crystallization) $n_1 > n_0$ and $\eta_0 > 0$. For $1/\xi < q < q_c$ the value of the density at the front edge decreases as the n_1 front propagates into the initial phase. The front

motion $L(t)$ is initially linear in time and advances slower than the perturbation. After a sufficiently long time, the motion ceases as the initial perturbation is incorporated into the front. For a fluctuation with $q < 1 /\xi$, the profile edge $L(t)$ recedes and the n_1 phase vanishes . The value of the density at the profile edge increases with time to conserve particle number. A convective instability occurs; the localized perturbation grows while moving away from its initial location although at a fixed location it appears to decay.[9] The discussion is similar when the density of new phase is smaller than that of the initial phase (such as on evaporation or melting) with $n_1 < n_0$ and $\eta_0 < 0$.

The phase transition can be also induced by periodic deformation of the initial phase. Setting $q \rightarrow iq$, the dispersion relation $\omega(q)$ is obtained from (4). There is a critical wave vector Q_c with Im $\omega(Q_c) = 0$. The solution is a damped wave for a periodic fluctuation in the initial phase of small wave length or $q > Q_c$ and the initial profile is stable. For a wave length larger than the critical length or wave vector $q < Q_c$, the dispersion relation is real and positive and the solution is a front which advances as the periodic deformation decays.

The results can be applied to spherical geometry and the discussion of cluster dynamics follows the planar case. The linear stability of the classical cluster, defined as $n(r,t) = n_1$ $(r<a)$ and $n(r,t) = n_0$ $(r>a)$, to a local increase of density at the surface $r = a$ of the cluster proceeds as before. For a fluctuation $\eta(r,t) = 0$ for $r<a$ and $\eta(r,t) = \dfrac{\eta_0}{r}\exp[-qr + \omega t]$, $r>a$, which increases the density near the surface, the linear equation (4) is obtained in radial coordinates for the function $\eta(r,t)r$. For stationary particle number, the dynamics of the cluster radius a is given by the radial flux at the surface: $da/dt = - j_r (a,t) /(n_1-n_0 -\eta (a,t))$ [4]. The cluster is stable and damped vibrations are induced for $q > q_c$. For $1/\xi < q < q_c$, front propagation sets in, the cluster will start to grow with a decreasing density at the cluster surface[10]. For an initial thick layer of width $q<1/\xi$, the cluster is unstable with possibly a transition to nonspherical shapes. In contrast, for the solution described in [11], the unfavorable surface to bulk ratio always inhibits growth in small clusters .

CONCLUSIONS

In experiments or numerical simulation, the boundary and initial conditions within the cell determines the dynamics observed. To start a phase transition by wetting, the parameters of importance are ξ^{-1} and $\xi\beta/c_0$ in the initial phase. If favorable, a large range of possible fluctuations causes the initial phase to become dynamically unstable and propagation and growth of the new phase sets in. Vibrations are excited for small scale initial fluctuations at the onset of a phase transition. In real systems, a complex signal will emerge but the resulting turmoil dies down after β^{-1}. The characteristic time is sufficiently long in polymer systems to freeze the transient states, resulting in small scale periodic micro- or nanostructures .

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